

Unusual superparamagnetic behavior of Co_3O_4 nanoparticles

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We report detailed studies on magnetic properties of Co_3O_4 nanoparticles of average size 12.5 nm. Temperature and field dependence of magnetization, wait time dependence of magnetic relaxation (aging), memory effects and temperature dependence of specific heat have been investigated to understand the magnetic behavior of these particles. We find that the particles show some features characteristic of nanoparticle magnetism such as bifurcation of field cooled (FC) and zero field cooled (ZFC) susceptibilities and a slow relaxation of magnetization. However, strangely, the temperature at which ZFC magnetization peaks coincides with the bifurcation temperature and does not shift on application of magnetic fields up to 1 kOe, unlike most other nanoparticle systems. Aging effects in these particles are negligible in both FC and ZFC protocol and memory effects are present only in FC protocol. Our results show that Co_3O_4 nanoparticles constitute a unique system where superparamagnetic blocking starts above the Néel temperature, in the paramagnetic state.

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I. INTRODUCTION

In the past two decades, magnetic nanoparticles have attracted much attention due to (1) their potential uses in various areas such as data storage and biomedicine and (2) the challenge to understand the physics underlying the various exotic phenomena exhibited by them.^{1,2} Most of such work has focussed on ferromagnetic and ferrimagnetic nanoparticles because of their high magnetic moments that make them industrially valuable. However, there have been a few studies on antiferromagnetic nanoparticles and interestingly, their magnetic behavior is found to be more complex and intriguing.

Below a critical size, particles of a ferromagnetic or ferrimagnetic material consist of a single domain and each particle carries a magnetic moment, which can reverse its direction due to thermal agitation. In these particles, the magnetic dynamics is thermally activated leading to paramagnetic behavior above a particular temperature, called blocking temperature. Below this temperature, the moments appear blocked in a particular direction, on the time scale of the measurement. This phenomenon is known as superparamagnetism as instead of atomic spins, particle moments ("superspins") are involved. Thus ferromagnetic nanoparticles are expected to show superparamagnetism, though, interparticle interactions can complicate matters leading to spin glass like behavior.³⁻⁸ Antiferromagnetic nanoparticles can also develop a net moment due to uncompensated spins and can exhibit superparamagnetism as proposed by Néel.^{9,10} However, surface effects can also be important in the determination of their magnetic behavior and spin glass like behavior can arise due to freezing of spins at the surface in addition to interparticle interactions.¹¹

Magnetic nanoparticles show some characteristic features which are common to both spin glasses and superparamagnets. These include irreversibility in the field cooled (FC) and zero field cooled (ZFC) magnetizations,

a peak in ZFC magnetization, slow magnetic relaxation and hysteresis at low temperature. However, some important features that distinguish these two are: (1) FC magnetization goes on increasing as the temperature is decreased in superparamagnets while it tends to saturate below the freezing temperature in particles showing spin glass behavior.⁵ (2) In systems showing spin glass like behavior, wait time dependence of relaxation (aging) and memory effects are present in both FC and ZFC magnetizations. In contrast, in superparamagnetic particles, these effects are present in FC magnetization only.^{3-8,12-16} (3) The field dependence of temperature at which the ZFC magnetization peaks (T_P) is known to behave differently in the two cases.^{11,17-19}

There have been studies on various antiferromagnetic nanoparticles in both bare and coated forms in the past several years and there is a lot of variation in the magnetic behavior of different materials. NiO nanoparticles have been reported to show spin glass like behavior;^{3,11} CuO nanoparticles show an anomalous magnetic behavior that cannot be described as superparamagnetic or spin glass like;²⁰ Ferritin shows superparamagnetic behavior;^{5,21} etc. Co_3O_4 is an antiferromagnetic material and in the bulk form, its Néel temperature has been reported to lie between 30 K and 40 K.²² There have been some reports on hysteresis, time dependence of magnetization, exchange bias and finite size effects in bare, coated and dispersed Co_3O_4 nanoparticles and various conflicting claims have been made in support of spin glass like and superparamagnetic behavior in these particles.²²⁻³¹ It will be, therefore, worthwhile to investigate their magnetic behavior carefully. In the present work, we present temperature and field dependence of magnetization, aging and memory effects and specific heat measurements on Co_3O_4 nanoparticles.

II. EXPERIMENTAL DETAILS

Co_3O_4 nanoparticles are prepared by a sol gel method. Aqueous solution of sodium hydroxide is mixed with that of cobalt nitrate till the pH of the solution becomes 12. At this stage cobalt hydroxide separates from the solution forming a gel that is centrifuged to obtain a precipitate which is washed with water and ethanol several times and dried to obtain a precursor. This precursor is heated at 250°C for 3 hours to obtain Co_3O_4 nanoparticles. The sample is characterized by X-ray diffraction (XRD) using a Seifert diffractometer with $\text{Cu K}\alpha$ radiation. The average particle size as estimated from the broadening of XRD peaks using the Scherrer formula comes out to be 12.5 nm. All the magnetic measurements are done with a SQUID magnetometer (Quantum Design). Specific heat measurements are done with a PPMS (Quantum Design).

III. RESULTS AND DISCUSSION

A. Temperature and field dependence of magnetization

The temperature dependence of magnetization was done under field cooled (FC) and zero field cooled (ZFC) protocols at fields 100 Oe, 300 Oe and 1000 Oe. See Figure 1. We note that the FC magnetization in this case is increasing with decrease in temperature down to the lowest temperature of measurement without any sign of saturation, a feature characteristic of superparamagnets.⁵ However, the temperature at which ZFC magnetization peaks (31 K) i.e. T_P is also the temperature of bifurcation (T_{bf}) of FC and ZFC magnetizations.³² Strangely, in this case, T_P is independent of the magnetic field applied and the dc susceptibility data taken for different fields superpose. This is in contrast to other nanoparticles where the peak temperature is found to shift to lower temperatures on increasing the field even at fields as low as a few hundred Oerstedes.^{11,17–19,33,34} Another distinct feature in Figure 1 is a sudden change in the slope of FC magnetization curve at the peak temperature. This will be discussed later in subsection D.

We have done hysteresis measurements at 5 K and a magnified view is shown in the inset of Figure 1. The virgin curve in this case is a straight line in contrast to spin glasses where it is usually S-shaped.³⁵

B. Néel temperature

When the particle size of an antiferromagnetic material is decreased to nanoscale, its Néel temperature (T_N) is known to decrease significantly due to finite size effects.^{27,36} We carried out specific heat measurements on pelletized nanoparticles to make an estimate of T_N and these data are presented in the inset of Figure 2. It can be observed that the specific heat decreases linearly

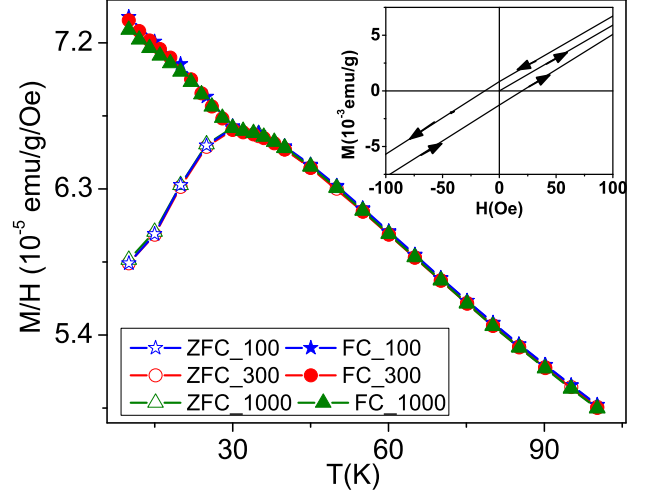


Figure 1: (Color online) Temperature dependence of FC and ZFC susceptibilities at 100 Oe, 300 Oe and 1000 Oe. Inset shows the hysteresis at 5 K.

with decrease in temperature down to 35 K below which it increases with a peak at 28 K. We have calculated the magnetic specific heat by subtracting a linear contribution from the total specific heat and this data has been shown in the main panel of Figure 2. It can be seen that a magnetic contribution is noticeable between 15 K and 40 K with a peak at 26 K, which should correspond to the Néel temperature.

In some works on antiferromagnetic nanoparticles, T_N

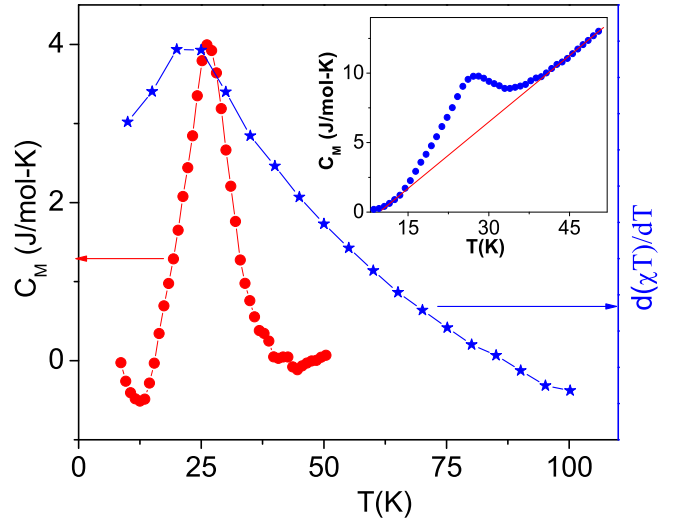


Figure 2: (Color online) Magnetic contribution to specific heat estimated by subtracting the linear component at lower temperatures and plot of $d(\chi T)/dT$ as a function of temperature. Inset shows the plot of specific heat as a function of temperature. The line (red) shows the linear part of specific heat which is subtracted from total specific heat to get the magnetic contribution.

has been identified as the temperature of the peak of $d(\chi T)/dT$ vs T curve.^{31,37} This is in accordance with Fisher's equation relating specific heat (C) and magnetic susceptibility (χ):³⁸

$$C \propto d(\chi T)/dT \quad (1)$$

This relation has been verified experimentally for some bulk materials.³⁹ It will be interesting to check this relation for the present nanoparticle sample. In Figure 2, we have also shown the plot of $d(\chi T)/dT$ as a function of T , which has a peak somewhere in between 20 K to 25 K, giving an estimate of the Néel temperature. Thus the value of T_N extracted from the specific heat is somewhat greater than the value obtained from the Fisher relation.

C. Aging and memory effects

Nanoparticles that show spin glass like behavior are expected to show aging and memory effects in both FC and ZFC protocols while those showing superparamagnetic behavior show these effects only in FC protocol. Further the effects in FC protocol are weaker in superparamagnetic particles than in those showing spin glass like behavior.³⁻⁵ These experiments can thus give valuable information about the nature of magnetic behavior of a system.

For doing aging experiments in FC protocol, the sample is cooled to a particular temperature in a field of 100 Oe, the field is switched off after waiting for a specified period and magnetization is recorded as a function of time. In the corresponding ZFC case, the sample is cooled to the temperature of interest in zero field and the field is switched on after a certain wait time and subsequently magnetization is recorded as a function of time. We show the results of aging experiments at 20 K in Figure 3. It can be seen that aging effects are negligible in both FC and ZFC measurements.

For carrying out FC memory experiments, the system is cooled in the presence of a magnetic field to 20 K and a stop of one hour is taken at this temperature. Magnetic field is switched off for the duration of the stop and is turned on before further cooling the sample to 10 K. The magnetization is measured while cooling and then during subsequent heating. These data have been taken at 300 Oe field. See Figure 4. It can be observed that there is some indication of memory as the heating curve meets the cooling curve just after the temperature at which the stop was taken. We have also done memory experiments in ZFC protocol with a stop of one hour at 20 K and did not find any indications of memory. See the inset of Figure 4. In this case, ΔM is less than 0.05% as opposed to canonical spin glasses or nanoparticle systems that show spin glass like behavior where differences of order 1% or more are observed.^{3,40}

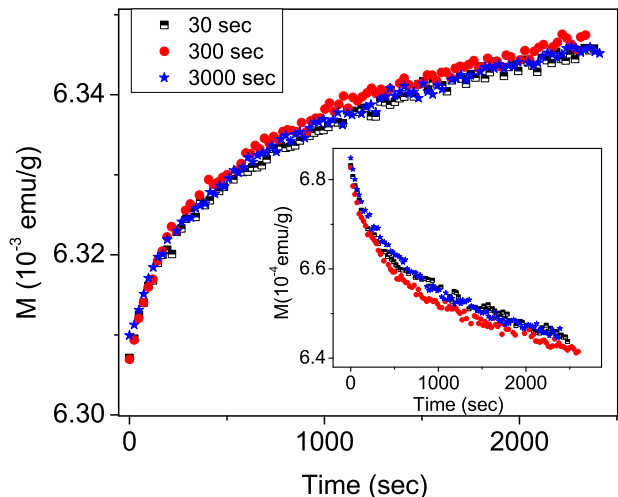


Figure 3: (Color online) Aging experiments in ZFC protocol at 20 K with waiting times 30 s, 300 sec and 3000 sec. Inset shows the corresponding experiments in FC protocol.

D. DISCUSSION

Co_3O_4 nanoparticles show some features characteristic of nanoparticle magnetism. Some of these are due to finite size effects viz. a net magnetic moment due to uncompensated surface spins and a decrease in Néel temperature. Some are manifestations of non equilibrium in magnetic nanoparticles and are common to both superparamagnetic and spin glass like behaviors. These include irreversibility in FC and ZFC magnetization and

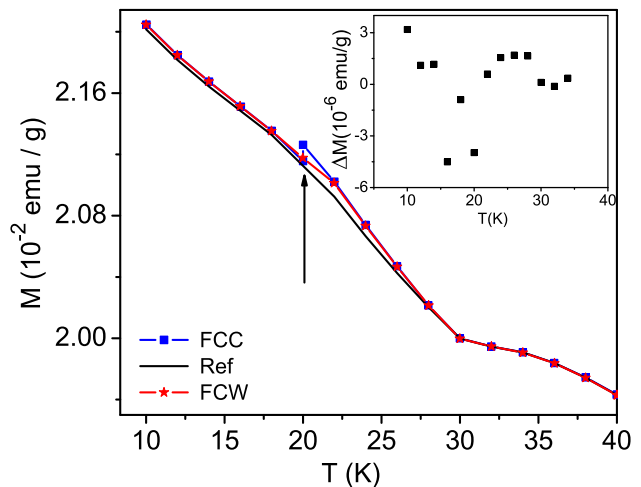


Figure 4: (Color online) Memory experiments in FC protocol with a stop of one hour duration at 20 K at a field of 300 Oe. The field is switched off during the stop (shown as arrow). Inset shows the corresponding data for ZFC memory experiment. The difference in magnetization with a stop of one hour at 20K in the cooling process and the reference data is plotted as a function of temperature.

a slow magnetic relaxation at low temperature. However there are several unusual features observed in this system, that deserve a second look.

1. Behavior above T_P

In ferromagnetic and ferrimagnetic nanoparticles, the ZFC magnetization generally shows a peak at a particular temperature, above which the behavior is superparamagnetic i.e. magnetization curves taken at various temperatures above T_P superpose when plotted against H/T .⁴¹ Makhlof et al. have shown that magnetization vs $H/(T+\theta)$ curves superpose at high temperatures in Co_3O_4 nanoparticles ($\theta = 85$ K), a feature characteristic of antiferromagnets.²⁶ Our data (50 K-300 K) also fits well to Curie-Weiss law, $\chi \propto 1/(T + \theta)$, with $\theta = 107$ K and coefficient of determination, $R^2 = 0.9992$. Further, T_P is independent of applied field in contrast to nanoparticles showing superparamagnetism. The preceding discussion implies that the system is not superparamagnetic above T_P and the peak in ZFC magnetization is a signature of a transition from paramagnetic to antiferromagnetic state. It may be noted that T_N as found by specific heat measurements is 5 K less than T_P and the Fisher relation gives an even lower estimate of T_N . We note in passing that similar observation of $T_N < T_P$ has been reported earlier.^{31,39}

At T_P , there also occurs a bifurcation between FC and ZFC magnetization and this change looks abrupt as at this point a slope change in the FC magnetization can be seen. Thus even before the actual transition to an antiferromagnetic state, the particles develop a magnetic moment and go to a blocked state. This may be due to the short range antiferromagnetic correlations which are known to persist above the Néel temperature.⁴² These short ranged correlations can give rise to a net magnetic moment when the correlation length becomes comparable to the particle size and thus the particles can get blocked above T_N .

2. Behavior below T_P

There have been some reports of spin glass like features in Co_3O_4 nanoparticles coated with organic surfactants and those dispersed in amorphous matrices at low temperature.^{22,28-30} However, in the present work and in other studies on bare nanoparticles, no such features have been found.^{26,31} Absence of aging and memory effects in ZFC protocol confirms that the behavior of Co_3O_4 nanoparticles is not spin glass like.^{3,5,14,15} Thus below T_P , observation of a bifurcation in FC and ZFC magnetizations and slow relaxation of magnetization seems to correspond to a blocked state as observed in superparamagnetic particles. Presence of memory effects in FC protocol also support this inference.

The blocking temperature in superparamagnets is known to be field dependent, but in this case it is independent of field at least up to fields of 1 kOe. In superparamagnetic particles, the particle moment can have two directions along an axis determined by anisotropy. In zero field, these two states are separated by an energy barrier and are equally likely to be occupied. Application of a magnetic field breaks the degeneracy of these two states, making it easier for the particle to go from the higher energy state (antiparallel to field) to the lower energy state (parallel to field). At a particular temperature, if the thermal energy available is insufficient for crossing this barrier, the particles will be in a blocked state. We propose that in the present case, particles develop a magnetic moment at T_P and immediately get blocked with an energy barrier greater than $k_B T_P$. The applied magnetic fields (up to 1 kOe in this case) are not sufficient to decrease the barrier significantly so that the particles are not able to get unblocked at this temperature. Hence the blocking temperature in this case is independent of field.

Another unique feature observed in this system is that the ZFC susceptibilities taken at different fields lie on the same curve while there is a slight mismatch between corresponding FC susceptibilities. This is due to the fact that in ZFC measurement the system is cooled in a zero field and then a field is applied at low temperature to measure the magnetization, and thus the corresponding values of magnetization lie on the virgin curve of hysteresis loop which is a straight line with zero intercept ($M/H = \text{constant}$). However in FC measurements, the system is cooled in the presence of a field, and hence the magnetization values do not lie in the virgin curve, leading to slightly different susceptibilities at different fields.

IV. CONCLUSION

We have done a detailed study of the magnetic behavior of Co_3O_4 nanoparticles. We find that their behavior is unique among antiferromagnetic nanoparticles. There is a peak in ZFC magnetization and at this temperature (T_P), a sudden bifurcation between FC and ZFC magnetization occurs. Strangely, this temperature lies above the Néel temperature as estimated by specific heat measurements and a sudden slope change in FC magnetization is seen at this point. The behavior of susceptibility above the peak temperature is paramagnetic rather than superparamagnetic and Curie-Weiss law holds as in the case of antiferromagnets. Further unlike other magnetic nanoparticles, T_P does not change with magnetic field. Aging and memory effects are not observed in ZFC magnetization measurements which show the absence of spin glass like behavior in this system. However observation of memory in FC protocol supports superparamagnetic blocking below T_P . This system undergoes a transition from paramagnetic to blocked state even before the transition to an antiferromagnetic state and we ascribe this

to antiferromagnetic correlations present above Néel temperature.

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